Temperature Dependence of the ^{127}I-Nuclear Quadrupole Coupling in Tetramethylammonium-periodate $(CH_3)_4NIO_4$

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Z. Naturforsch. **39 a,** 1222–1224 (1984); received October 16, 1984

Tetramethylammonium-periodate shows ^{127}I-NMR second order quadrupole splitting with negative temperature coefficients α for the quadrupole coupling constants and a second order phase transition. From these measurements one can exclude the ratio $(r_{\text{cation}}/r_{\text{anion}}) > 1$ to be the origin of the anomalous temperature dependence in NH_4IO_4.

1. Introduction

With the identification of anomalous positive temperature coefficients α for the quadrupole coupling constants e^2qQ/h and consequently for the electric field gradients in certain ammonium salts, for example NH_4ReO_4, ND_4ReO_4 and NH_4IO_4 [1–4], some attempts were made to explain these observations discussing the reorientational behaviour of NH_4^+, static effects or anomalous temperature dependence of the lattice parameter a, the basis length of the elementary cell [1, 5, 6]. The title compound $(CH_3)_4NIO_4$ was the first meta-periodate with a ratio $(r_{\text{cation}}/r_{\text{anion}}) > 1$ showing second order quadrupole effects in its solid state ^{127}I-NMR spectra. In the temperature range $301\ \text{K} < T < 418\ \text{K}$ we found a normal, but extremely large negative temperature coefficient α for the ^{127}I-quadrupole coupling constants [7]. This challenged us to further ^{127}I-NMR measurements of $(CH_3)_4NIO_4$ at lower temperatures in order to exclude the ratio $(r_{\text{cation}}/r_{\text{anion}}) > 1$ to be responsible for anomalous quadrupole temperature coefficients.

2. Experimental

The ^{127}I-NMR powder spectra of tetramethylammonium-periodate [8] measured with a Bruker FT-NMR CXP 200 spectrometer between 200 K and 300 K are depictured in Figure 1. The last spectrum at 300 K shows the typical second order ^{127}I-NMR quadrupole splitting of the central ^{127}I-NMR transi-

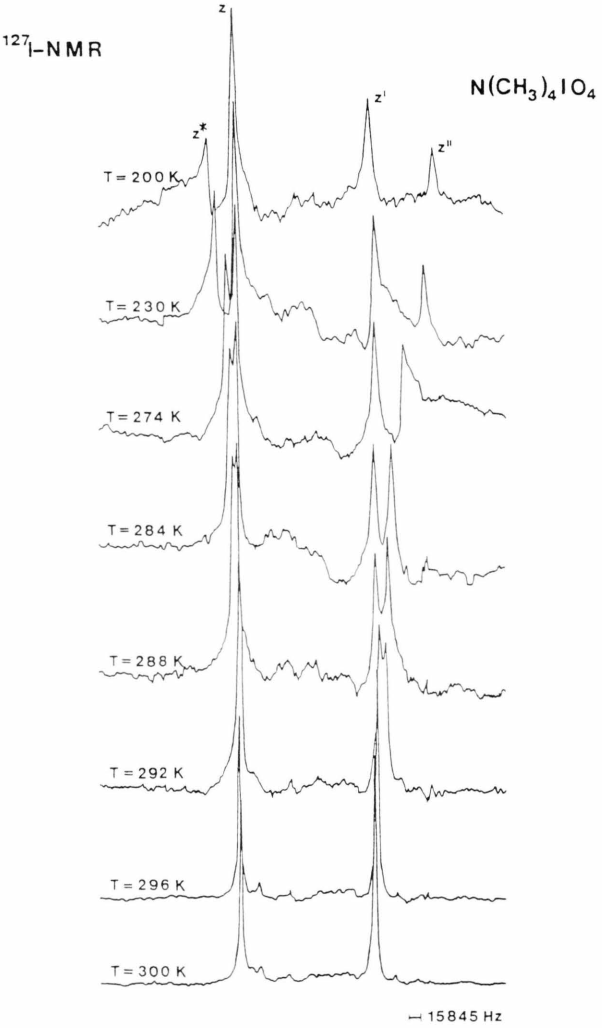

Fig. 1. ^{127}I-NMR signals with second order quadrupole splittings of $(CH_3)_4NIO_4$ measured between 200 K and 300 K.
Sweep range: SW = 625000 Hz; Pulse program: one cycle pulses; Pulse width: 3 μs; Recycle time: 30 ms.

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tion $(+1/2 \leftrightarrow -1/2)$ with asymmetry parameter $\eta \to 0$. All other spectra with temperatures below $T = 296$ K have additional signals arising from a further quadrupole splitting.

3. Results and Discussion

When lowering the temperature, at least one of the quadrupole coupling constants increases because there are two possibilities in calculating the quadrupole splittings $\Delta\nu_n$:

Case A with $\Delta\nu_1 = z^* \to z'$ and $\Delta\nu_2 = z \to z''$,
Case B with $\Delta\nu_3 = z \to z'$ and $\Delta\nu_4 = z^* \to z''$.

By knowing the ^{127}I-Larmor precession frequency ν_L at the field $B_0 = 4.698$ T and the measured values of $\Delta\nu_n$ for the respective temperatures the quadrupole coupling constants can be calculated for the asymmetry parameter $\eta = 0$. The results for $(CH_3)_4NIO_4$ are shown in Table 1 and Fig. 2, which lead to the following conclusions:

(i) Independently of the two possible cases the diagram (Fig. 2) shows the appearance of a second phase at $T < 296$ K. The quadrupole coupling constants of this low temperature phase are in the order of 15 to 20 MHz and all ^{127}I-quadrupole interactions of $(CH_3)_4NIO_4$ have a normal temperature dependence with a negative temperature coefficient α. This means that the condition $r((CH_3)_4N^+) > r(IO_4^-)$ does not cause anomalous temperature coefficients of the ^{127}I-quadrupole coupling constants.

(ii) A second order phase transition is present independently of the two possible assignments, because there is a continuous change of the high temperature modification of the tetragonal crystal structure [8]. This will change the symmetry properties in the lattice and create two inequivalent positions of the iodine atoms.

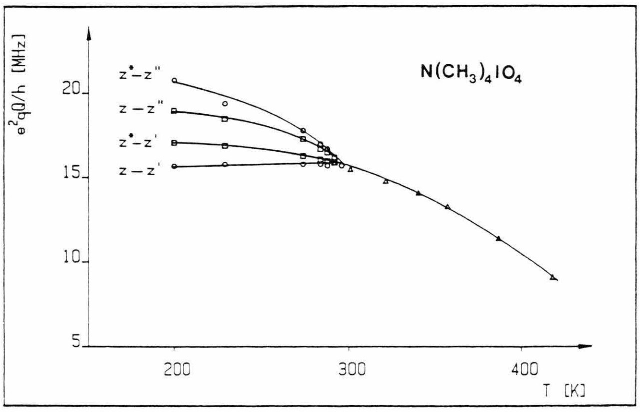

Fig. 2. Temperature dependence of ^{127}I-quadrupole coupling constants e^2qQ/h measured by second order quadrupole effects in ^{127}I-NMR powder spectra of $(CH_3)_4NIO_4$ for the cases A and B (see Table 1). Values e^2qQ/h for $T > 300$ K from our measurements loc. cit. [10].

Tab. 1. Temperature dependence of second order ^{127}I-NMR quadrupole splitting $\Delta\nu$ of $(CH_3)_4NIO_4$. The quadrupole coupling constants e^2qQ/h are calculated [9] with $\eta = 0$ for both cases A and B using $e^2qQ/h = 4\sqrt{2}\sqrt{\Delta\nu_n \cdot \nu_L}$; $\nu_L = {}^{127}$I-Larmor frequency at $B_0 = 4.698$ T.

T[K]	Case A $\begin{matrix} z \to z'' \\ z^* \to z' \end{matrix}$				Case B $\begin{matrix} z \to z' \\ z^* \to z'' \end{matrix}$			
	$\Delta\nu_1$ [kHz] $z^* \to z'$	e^2qQ/h [MHz] $z^* \to z'$	$\Delta\nu_2$ [kHz] $z \to z''$	e^2qQ/h [MHz] $z \to z''$	$\Delta\nu_3$ [kHz] $z \to z'$	e^2qQ/h [MHz] $z \to z'$	$\Delta\nu_4$ [kHz] $z^* \to z''$	e^2qQ/h [MHz] $z^* \to z''$
300	–	–	–	–	188.0	15.5	–	–
296	–	–	–	–	192.3	15.7	–	–
292	195.9	15.9	205.7	16.2	195.9	15.9	205.7	16.2
288	198.3	16.0	211.2	16.5	192.9	15.7	216.7	16.7
284	201.4	16.1	217.9	16.7	193.5	15.8	225.8	17.0
274	206.9	16.3	233.8	17.3	193.5	15.8	247.2	17.8
230	221.5	16.9	265.5	18.5	194.1	15.8	293.0	19.4
200	227.7	17.1	280.8	19.0	191.6	15.7	316.8	20.8

(iii) An extrapolation of the known e^2qQ/h-curve (△△△) into the region $T < 300$ K (see Fig. 2) runs through the average values of the quadrupole coupling constants calculated from the two possible cases A and B. From our measurements it is impossible to decide, which of the two cases correctly describes the behaviour in the lattice, where obviously two sorts of distorted IO_4^--tetrahedrons exist. With case B one of the IO_4^--tetrahedra is provided with a small electric field gradient, which is independent of temperature (lower curve ○○○). The other has a larger electric field gradient, which is temperature dependent. Consequently the IO_4^--tetrahedron is more distorted. If case A prevails, one group of the IO_4^--tetrahedrons changes its field gradient at the iodine atom in the same way as the high temperature modification. This can be seen in Fig. 2, where the △-curve passes continuously into the lower □-curve. For the other IO_4^--tetrahedron one observes an insignificantly larger electric field gradient. In this prefered version there are smaller deviations in the lattice. Further studies of $(CH_3)_4NIO_4$ together with another group [11] are in progress.

Acknowledgement

We wish to express our gratitude to Professor H. P. Fritz, Institute of Inorganic Chemistry, Technical University of Munich, for financial support of this research.

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